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Low Temperature Performance of Selective Catalytic Reduction of NO with NH_3 under a Concentrated CO_2 Atmosphere

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Received: 24 September 2015 ; Accepted: 22 October 2015 ; Published: 30 October 2015
Academic Editor: Vasily Novozhilov

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Abstract: Selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) has been widely investigated to reduce NO_x emissions from combustion processes, which cause environmental challenges. However, most of the current work on NO_x reduction has focused on using feed gas without CO_2 or containing small amounts of CO_2. In the future, oxy-fuel combustion will play an important role for power generation, and this process generates high concentrations of CO_2 in flue gas. Therefore, studies on the SCR process under concentrated CO_2 atmosphere conditions are important for future SCR deployment in oxy-fuel combustion processes. In this work, Mn- and Ce-based catalysts using activated carbon as support were used to investigate the effect of CO_2 on NO conversion. A N_2 atmosphere was used for comparison. Different process conditions such as temperature, SO_2 concentration, H_2O content in the feed gas and space velocity were studied. Under Mn-Ce/AC conditions, the results suggested that Mn metal could reduce the inhibition effect of CO_2 on the NO conversion, while Ce metal increased the inhibition effect of CO_2. High space velocity also resulted in a reduction of CO_2 inhibition on the NO conversion, although the overall performance of SCR was greatly reduced at high space velocity. Future investigations to design novel Mn-based catalysts are suggested to enhance the SCR performance under concentrated CO_2 atmosphere conditions.

Keywords: selective catalytic reduction (SCR); oxy-fuel combustion; low-temperature; Mn; Ce; CO_2

1. Introduction

NO_x emissions are responsible for acid rain and urban smog, and they pose a significant risk to the environment and human health [1]. Selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) has been extensively investigated and also been used commercially for NO_x reduction. The industrial operation is based on V_2O_5-WO_3 (MoO_3)/TiO_2 catalysts, which are reactive within a high temperature window (300–400 °C) [2–4]. However, many pollutants, e.g., sulphur and dusts, are present in this reactive temperature range, causing the deactivation of selective catalytic reduction (SCR) catalyst [5]. Therefore, there is a strong need to develop catalysts for low temperature SCR processes, which can be placed after the electrostatic precipitator and desulfurizer to avoid pollutants such as sulphur and particulates.

Catalysts containing transition metals have been widely researched for low-temperature SCR, due to the effective catalytic ability of transition metals [6–10]. Among them, Mn- and Ce- based catalysts have drawn particular attention due to their abundant oxygen vacancies, which promote the redox cycle during SCR reactions [11–14]. In addition, activated carbon (AC) has been used as catalyst support for SCR, since it has high surface for metal loading and the presence of functional groups on the surface of activated carbon can also promote NO_x conversion [15–19].

Currently, NH_3-SCR is mostly investigated under N_2 atmospheres, to simulate the stationary NO_x sources of power plants. It is realized that oxy-fuel combustion is attracting increasing interest. Using pure oxygen instead of air for combustion generates a flue gas which consists of mainly CO_2 and H_2O, where CO_2 can be easily captured [20–23]. Therefore, more understanding of NH_3-SCR in the presence of an abundance of CO_2 is essential for the future development of SCR technology combined with oxy-fuel combustion processes. However, it is found that there are a few works investigating the influence of CO_2 on SCR [24,25]. For example, Kim *et al.* [24] studied the effect of CO_2 on SCR using a small pore zeolite copper catalyst; and reported that CuSSZ13 catalyst can be deactivated by 10% CO_2 at low temperatures (<300 °C). Magnusson *et al.* [25] studied the influence of 6% CO_2 during SCR, and found no significant influences. To our best knowledge, there is very limited work about the investigation of low-temperature SCR under high concentrations of CO_2, simulating the flue gas from oxy-fuel combustion processes.

Furthermore, it is known that SCR performance is significantly affected by the process conditions such as temperature, space velocity [26–28], concentrations of H_2O [25,29–31], and the presence of SO_2 [6,11,25,30,32,33]. For example, Magnusson *et al.* [25] investigated SCR using a marine based catalyst; they reported that higher space velocity (18,300 h^{-1}) resulted in a continuous decrease in catalytic activity, compared with space velocities of 6100 and 12,200 h^{-1}; in addition, they also reported that at temperatures higher than 300 °C, the catalyst showed a stable catalytic reactivity at different SO_2 concentrations, but a significant reduction of SCR activity was observed at a temperature of 250 °C for gas streams containing 250 and 750 ppm SO_2. The decrease of SCR activity with the increase of space velocity has also been reported by other researchers [26]. Pan *et al.* [30] reported that H_2O has a reversible negative effect on NH_3-SCR using a MnO_x/MWCNTs catalyst, while SO_2 was found to have an irreversible deactivation effect.

In this work, our main objective was to investigate the SCR performance under a concentrated CO_2 atmosphere. Mn-Ce/AC with different process conditions, including temperature, SO_2 and H_2O and also space velocity were used. In addition, the performance of SCR catalyst under CO_2 atmosphere was compared to an inert N_2 atmosphere at various process conditions.

2. Experimental

2.1. Catalyst Preparation

Activated carbon (AC, 40–60 mesh, Kecheng Novel Technology Co., Ltd. Beijing, China) was used as catalyst support. It was pre-treated under 67% concentrated HNO_3 for 1.5 h at 80 °C, and washed with deionized water to a pH about 7. The washed AC was dried at 110 °C for 12 h before using as catalyst support. Catalyst support (treated AC) was added to an aqueous solution (100 mL) containing the desired amount of $Mn(NO_3)_2$ and $Ce(NO_3)_3$. The solution was stirred for 3 h and left for 2 h without stirring. The precursor was dried at 100 °C for 12 h and finally calcined at 500 °C for 3 h in N_2 atmosphere. Catalysts with different metal additions were prepared in this work: Mn/AC catalysts contained 3, 7, and 9 wt% Mn, respectively; Ce/AC catalysts had a Ce content of 3, 7 and 9 wt%, respectively. Also 7 wt% (Mn-Ce)/AC catalysts were prepared with the following Mn/Ce ratios: 1:4, 1:2, 1:1 and 2:1. The catalysts prepared in this work have BET surface areas around 300 $m^2 \cdot g^{-1}$ and pore volumes of about 0.3 $cm^3 \cdot g^{-1}$.

2.2. Experimental System

NH_3-SCR tests were carried out in a fixed bed reaction system shown in Figure 1. Simulated gases (NO, NH_3 and O_2 balanced with N_2 or CO_2) with a total flow rate of 1200 mL/min were introduced into the reaction system, where 2 g of catalyst was located. The catalysts were tested at temperatures between 100 °C and 300 °C. The NO concentration was analysed by a Flue Gas Analyzer (350 XL, Testo, Schwarzwald, Germany) The NO conversion was calculated using the following equation:

$$NO_{\text{conversion}}\% = \frac{[NO]_{\text{inlet}} - [NO]_{\text{outlet}}}{[NO]_{\text{inlet}}} \times 100\% \tag{1}$$

where $[NO]_{\text{inlet}}$ is the introduced NO concentration, vol%; $[NO]_{\text{outlet}}$ is the NO concentration in the outlet of the reactor, vol%.

In addition, the influences of space velocity (3408–13,632 h^{-1}), SO_2 content (0–400 ppm) and H_2O content (0%–8%) were also investigated under both CO_2 and N_2 atmospheres.

2.3. Catalyst Characterization

X-ray diffraction (XRD, Bruker, Karlsruhe, Germany) with monochromatized Cu Kα radiation was used to obtain the crystal structure of the fresh catalyst with scanning speed of 12 min^{-1} from 10° to 60°. Scanning electron microscopy (SEM, S-3500N, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM) (Tecnai-20, Royal Philips, Amsterdam, Netherlands) were used to obtain morphologies of the fresh catalysts. BET surface area and porosity of the fresh catalyst were determined using ASAP2020 equipment (Micromeritics, Norcross, GA, USA); during the analysis, a 0.2 g sample was first degassed under 150 °C before being used for adsorption/desorption of N_2.

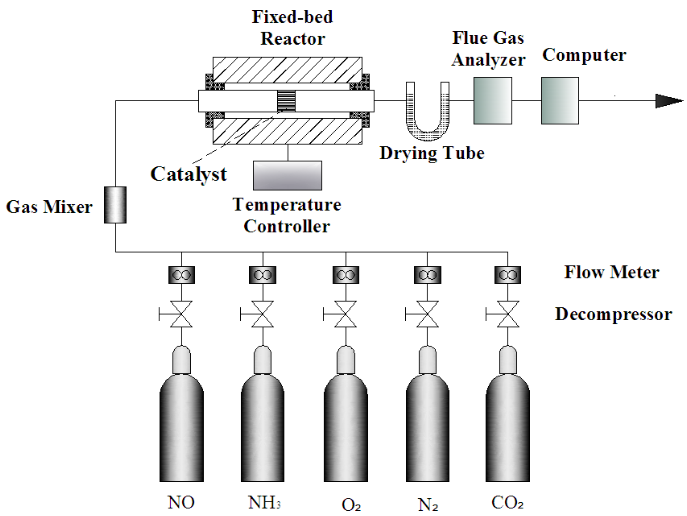


Figure 1. Schematic diagram of the selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) reaction system.

3. Results and Discussion

3.1. Comparison of CO_2 and N_2 Atmosphere with Different Catalysts

NH_3-SCR was carried out at temperatures between 100 °C and 300 °C with Mn/AC, Ce/AC and Mn-Ce/AC catalysts, respectively. As shown in Figure 2, activated carbon (AC) without metal loading showed very low NO reduction activity, with about 35% NO conversion. In addition, with little catalytic impact from catalyst (only using AC), CO_2 showed inhibition of NO conversion in the SCR test.

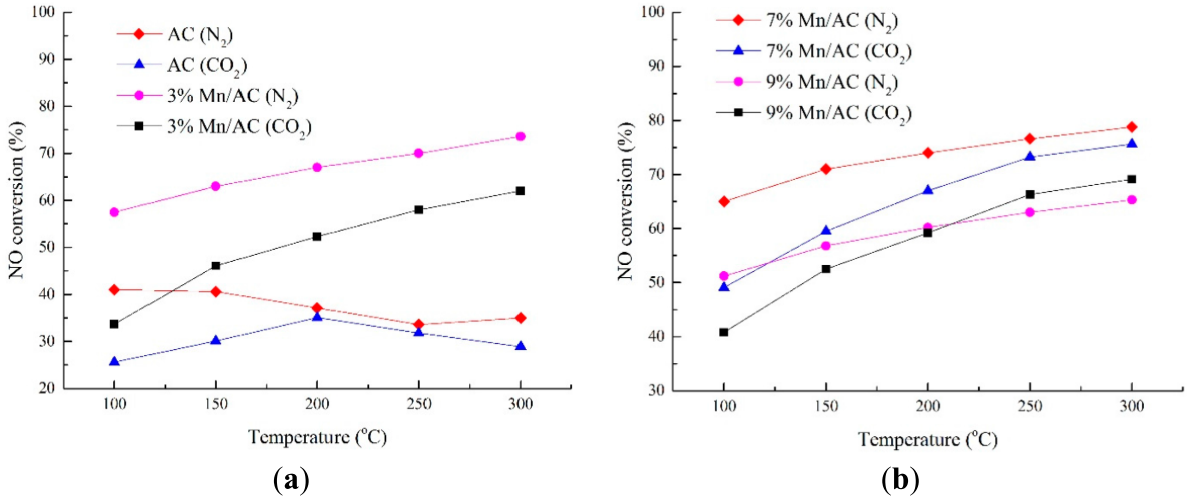


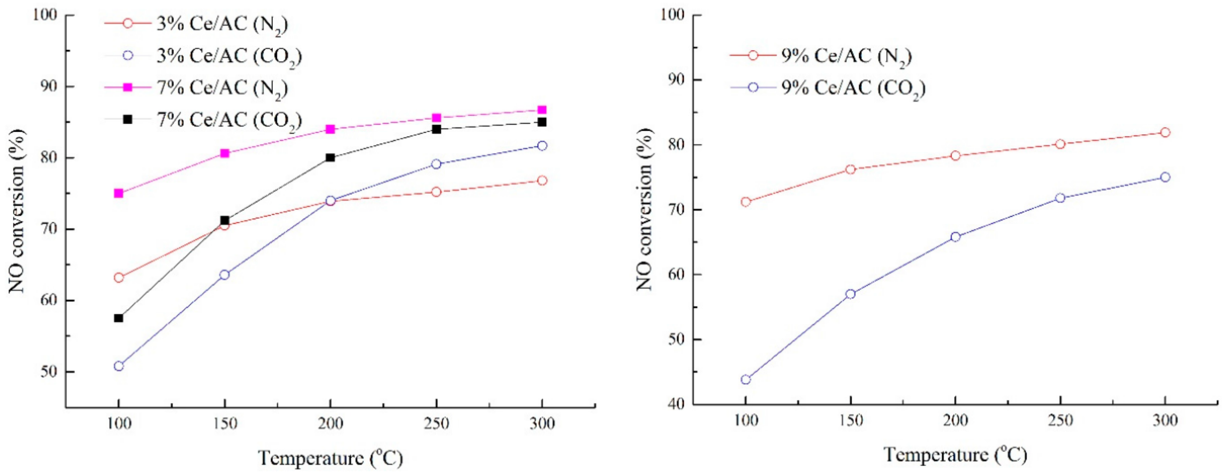
Figure 2. NH_3-SCR using Mn/AC catalyst under CO_2 and N_2 atmosphere. Other conditions: 800 ppm NO; 800 ppm NH_3, 6% O_2 and space velocity 3408 h^{-1}.

With the increase of reaction temperature from 100 °C to 300 °C, NO conversion was increased significantly in the presence of Mn/AC catalyst, for both N_2 and CO_2 atmospheres. The enhanced NO conversion at a relatively higher temperature using Mn-based catalyst has been reported [34–37]. Similar results were also found while using other catalysts (Figures 3 and 4).

From Figure 2, the conversion of NO was between 58% and 70% in the presence of 3% Mn/AC catalyst under N_2 atmosphere; the NO conversion was much lower in the CO_2 atmosphere (33%–58%). Using 7% Mn/AC catalyst, the N_2 atmosphere also gave higher NO conversion (65%–75%) compared with the CO_2 atmosphere (49%–70%). However, it seems that the difference of NO conversion between N_2 and CO_2 atmosphere was reduced at higher reaction temperatures, when the catalyst was changed from 3% Mn/AC (10% difference) to 7% Mn/AC (5% difference).

The advantage of N_2 atmosphere over CO_2 in terms of NO conversion was reduced when the Mn loading in the Mn/AC catalyst was increased to 9%. For example, the same level of NO conversion was observed from Figure 2 for both CO_2 and N_2 atmospheres at 200 °C using the 9% Mn/AC catalyst. When the reaction temperature was increased to 300 °C in the presence of the 9% Mn/AC catalyst, the NO conversion in the CO_2 atmosphere (69%) became higher than under the N_2 atmosphere (64%).

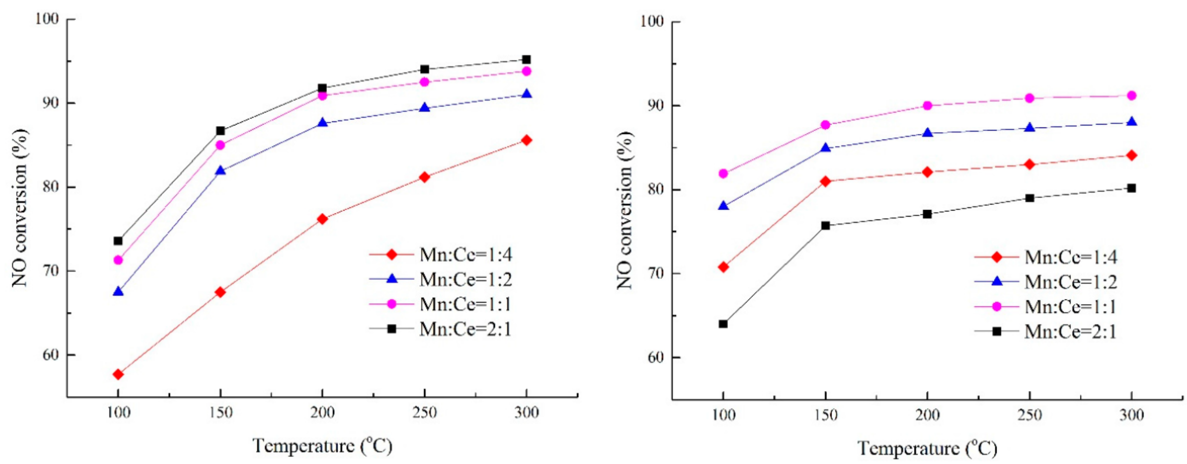
The NO conversion in relation to the reaction atmosphere has also been studied using Ce/AC catalysts. As shown in Figure 3, the difference of NO conversion between the CO_2 and N_2 atmosphere was also affected by the reaction temperature. When the reaction temperature was lower than 200 °C, the NO conversion was higher in the atmosphere of N_2 compared with the CO_2 one. When the reaction temperature was increased to 300 °C, in most of the cases, the N_2 atmosphere gave higher NO conversion compared with the CO_2 atmosphere; except when using the 3%Ce/AC catalyst, where the NO conversion was higher in the atmosphere of CO_2 (80%) compared with the N_2 one (75%).



(a) (b)

Figure 3. NH_3-SCR using Ce/AC catalyst under CO_2 and N_2 atmosphere: (**a**) 3% Ce/AC and 7% Ce/AC; (**b**) 9% Ce/AC. Other conditions: 800 ppm NO; 800 ppm NH_3; 6% O_2 and space velocity 3408 h^{-1}.

The SCR-NH_3 process was enhanced under the CO_2 atmosphere compared with the N_2 atmosphere, when the Mn loading in the catalyst was increased (Figures 2 and 3). This is consistent with the results shown in Figure 4, where the SCR experiments were carried out using Mn-Ce/AC catalysts with different Mn:Ce ratios. From Figure 4, catalyst with low Mn loading e.g., 7% Mn-Ce/AC (Mn:Ce = 1:4) showed a lower NO conversion in the CO_2 atmosphere (57%) compared with the N_2 atmosphere (71%) at the temperature of 100 °C.



(a) (b)

Figure 4. NH_3-SCR using different 7% Mn-Ce/AC catalysts under (**a**) CO_2 and (**b**) N_2 atmosphere. Other conditions: 800 ppm NO; 800 ppm NH_3; 6% O_2 and space velocity 3408 h^{-1}.

With the increase of Mn:Ce ratio, the NO conversion was increased for the CO_2 atmosphere, and fluctuated (increased first and then decreased) for the N_2 atmosphere. For example, the NO conversion was around 73% for the CO_2 and only 64% for the N_2 in the presence of the 7% Mn-Ce/AC (Mn:Ce = 2:1) catalyst at 100 °C. In addition, the overall performance of SCR was better in the CO_2 atmosphere compared with the N_2 atmosphere, when the catalyst has higher Mn:Ce ratio.

In summary, in this work we found that the depression of SCR activity under CO_2 atmosphere can be reduced by adding Mn metals in the catalyst system, while the presence of Ce in the catalyst enhanced the CO_2-induced SCR depression.

Mn-based catalysts have been widely researched for SCR, as various types of labile oxygen are present in the catalyst [38–40]. In addition, abundant oxygen vacancies present in amorphous Mn-based catalysts were reported to greatly improve the SCR activity [40]. The enhancement of SCR activity using Mn-based catalyst is also due to the promoted adsorption of NH_3 and NO oxidation to NO_2 [41], which play important roles in SCR [42]. In this work, it seems that amorphous Mn-species were present in the Mn-based catalyst; as shown in Figure 5, XRD analysis of the selected catalysts is presented. Diffraction peaks related to Mn or Ce metals could barely be observed, as little differences could be found from XRD analysis between AC and Mn-Ce/AC. The weak diffraction in the XRD analysis might be due to that the particle size of metal were very small. As shown in Figure 6 (TEM analysis), particles with size about 10 nm were observed in the fresh 7% Mn-Ce/AC (Mn:Ce = 1:4).

Kim *et al.* [24] reported that CO_2-induced deactivation in SCR was due to the adsorption of NH_3 by CO_2, and supression of the formation of nitrates, which are a key reaction intermediate for NO_x reduction. Yang *et al.* [43] also reported that CO_2 may compete for the adsorbed NH_3, which should be desirable for NO conversion.

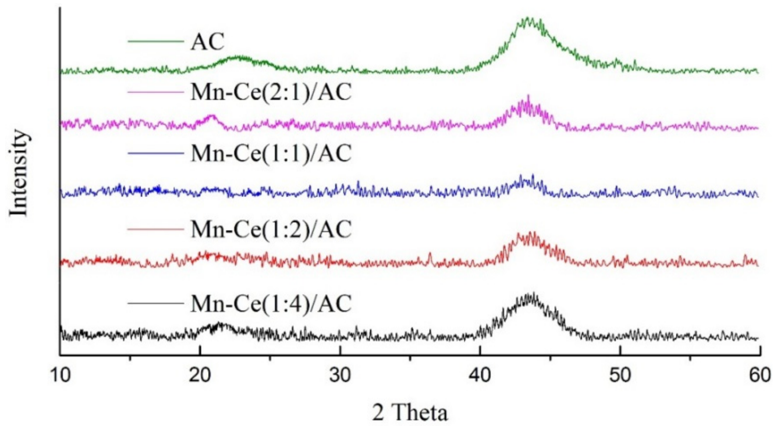


Figure 5. X-ray diffraction (XRD) analysis of the selected catalysts.

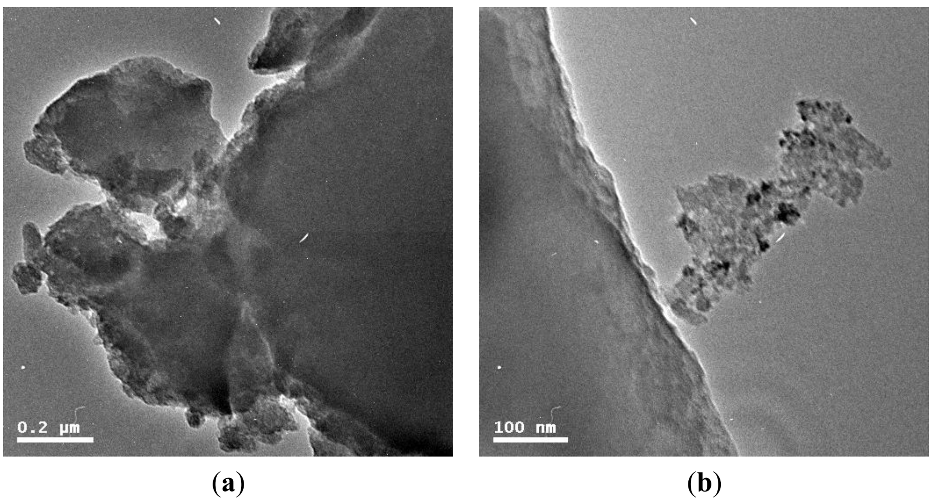


Figure 6. Transmission electron microscopy (TEM) analysis of the selected catalyst: (**a**) AC; (**b**) 7% Mn-Ce/AC (Mn/Ce 1:4).

Therefore, in order to reduce the negative effect of CO_2 in SCR, the adsorption of NH_3 by CO_2 should be depressed. In this work, we suggest that the formed Mn-based species might reduce the adsorption of NH_3 by CO_2. The addition of Mn in the catalysts changed some Lewis (weak) acid sites to Bronsted (strong) acid sites, which have been reported to be less affected by CO_2 [43]. It has also been reported that weak acid sites in the catalyst were changed into strong acid sites with the increase of Mn loading [8]. In addition, addition of Ce into MnTi catalyst resulted in an increase of Lewis acid sites, which enhances the inhibiting of CO_2 on SCR [43]; thus the literature supports the results obtained in this work, where catalysts with high Ce loading showed lower NO conversion under the CO_2 atmosphere compared with the N_2 atmosphere (Figure 4).

From the above results, we propose that the performance of SCR in CO_2 atmosphere is affected by the type of catalyst and also the reaction temperature. It is suggested that CO_2 has a more negative effect on SCR at low temperatures. In the following sections, we will discuss the influence of process conditions on SCR in the CO_2 and N_2 atmosphere.

3.2. Selective Catalytic Reduction of NO_x with NH_3 (NH_3-SCR) Test under CO_2 and N_2 Atmosphere with Different Process Conditions

The SCR performance under concentrated CO_2 was compared with a N_2 atmosphere under different process conditions. Figure 7 shows the effect of space velocity on the SCR performance using the 7% Mn/AC and the 7% Ce/AC catalysts. The higher space velocity resulted in a lower NO conversion might be due to the reduction of resisdence time of the reactants [25,26]. Although Ce-based catalyst has higher SCR activity compared with the Mn-based catalyst, we focus on discussions about the influence of the reaction atmosphere.

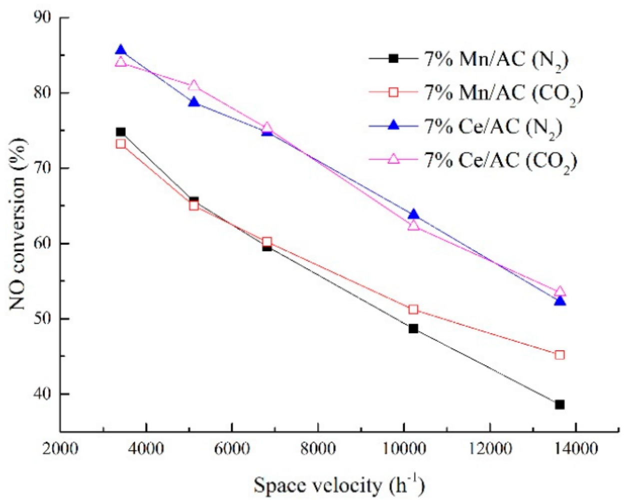


Figure 7. NH_3-SCR using different space velocity under CO_2 and N_2 atmosphere. Other conditions: temperature 250 °C; 800 ppm NO; 800 ppm NH_3 and 6% O_2.

From Figure 7, it seems that for the Mn/AC catalyst, higher NO conversion was observed under the CO_2 atmosphere compared with the N_2 atmosphere, under high space velocity (13,632 h^{-1}). The better SCR performance using CO_2 over N_2 was not observed in the presence of Ce/AC catalysts; this is consistent with the previous discussions that Mn reduces the negative effect of CO_2 while Ce does not. In addition, since the depression of SCR under CO_2 is mainly ascribed to the adsorption of NH_3 by CO_2, thus a higher space velocity could reduce/avoid the negative effects of CO_2. However, the overall NO efficiency could be greatly reduced at higher space velocity.

The influence of CO_2 atmosphere on SCR was also investigated under different SO_2 concentrations. SO_2 is known to have a negative effect on NO conversion due to catalyst poisoning [6,11,30]. As shown in Figure 8, for all of the tested three catalysts (Mn/AC, Ce/AC and

Mn-Ce/AC), the CO_2 atmosphere showed an inhibition of the NO conversion. In particular, the difference of NO conversion between CO_2 and N_2 atmosphere was increased with the increase of SO_2 concentration in the feed gas stream. For example, the NO conversion was similar for both CO_2 and N_2 atmosphere with the SO_2 concentration of 0 ppm; however, the N_2 atmosphere gave about 10% of NO conversion higher than the CO_2 atmosphere when the SO_2 concentration was increased to 400 ppm. Therefore, it is suggested that the presence of SO_2 enhances the inhibition of NO conversion in the CO_2 atmosphere.

The influences of a CO_2 atmosphere on catalytic SCR at different H_2O concentrations are shown in Figure 9. The increase of H_2O content from 0% to 8% resulted in a reduction of NO conversion for all the catalysts; this is consistent with the literature on the effect of H_2O addition [30,44]. It seems that the influence of H_2O concentration on NO conversion is small, when the CO_2 atmosphere is compared with the N_2 atmosphere, although a little higher NO conversion was observed for the N_2 atmosphere with 8% of H_2O. It is suggested that the presence of large amounts of H_2O, which would compete with NO and NH_3 adhering to the AC surface, has a more negative effect on the SCR performance in the CO_2 atmosphere, compared with the N_2 atmosphere.

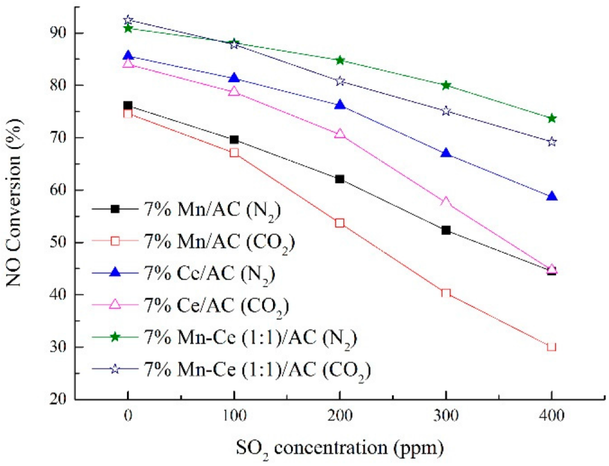


Figure 8. NH_3-SCR using different SO_2 concentrations under CO_2 and N_2 atmosphere. Other conditions: temperature 250 °C; 800 ppm NO; 800 ppm NH_3; 6% O_2 and space velocity 3408 h^{-1}.

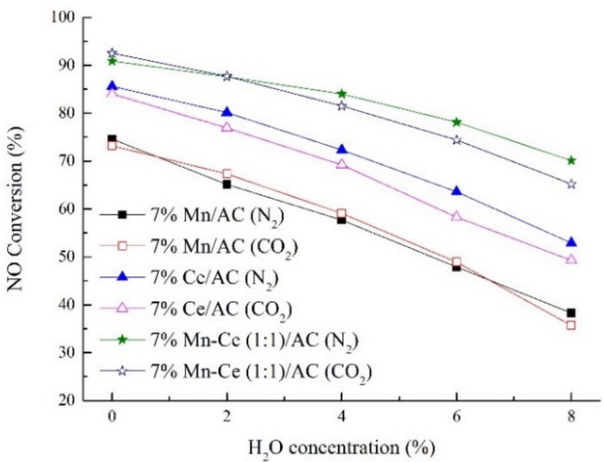


Figure 9. NH_3-SCR using different H_2O concentrations under CO_2 and N_2 atmosphere. Other conditions: temperature 250 °C; 800 ppm NO; 800 ppm NH_3; 6% O_2; 0 ppm SO_2 and space velocity 3408 h^{-1}.

4. Conclusions

In this work, the SCR process in the presence of Mn- and Ce-based catalysts under a concentrated CO_2 atmosphere was investigated in order to obtain information for developing SCR technologies combined with oxy-fuel combustion power plants. It is found that CO_2 can depress the conversion of NO, in particular at low reaction temperatures and with high SO_2 concentration in the feed gas. Under the Mn-Ce/AC catalysis conditions, the results showed that with the increase of Mn loading, the inhibitory effect of CO_2 on NO conversion was reduced, while adding Ce metal in the catalyst system enhanced the depression effect of CO_2 on SCR.

Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (Grant No. 51276055) and the Hebei Applied Basic Research Program of China (Grant No. 13964503D).

Author Contributions: Xiang Gou and Chunfei Wu conceived the research. Kai Zhang, Guoyou Xu, Meng Si and Xiang Gou carried out the experiment. Xiang Gou, Chunfei Wu, Kai Zhang, Guoyou Xu and Meng Si participated in the analysis of the data and writing the initial manuscript. Chunfei Wu, Xiang Gou, Yating Wang, Enyu Wang, Liansheng Liu and Jinxiang Wu revised the manuscript and adjusted the data presentation. All authors have read and approved the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, Z.; Woo, S. Recent Advances in Catalytic DeNO$_x$ Science and Technology. *Catal. Rev.* **2006**, *48*, 43–89. [CrossRef]
2. Wu, S.; Yao, X.; Zhang, L.; Cao, Y.; Zou, W.; Li, L.; Ma, K.; Tang, C.; Gao, F.; Dong, L. Improved low temperature NH_3-SCR performance of FeMnTiO$_x$ mixed oxide with CTAB-assisted synthesis. *Chem. Commun.* **2015**, *51*, 3470–3473. [CrossRef] [PubMed]
3. Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts: A review. *Appl. Catal. B Environ.* **1998**, *18*, 1–36. [CrossRef]
4. Amiridis, M.D.; Duevel, R.V.; Wachs, I.E. The effect of metal oxide additives on the activity of V_2O_5/TiO_2 catalysts for the selective catalytic reduction of nitric oxide by ammonia. *Appl. Catal. B Environ.* **1999**, *20*, 111–122. [CrossRef]
5. Liu, F.; Asakura, K.; He, H.; Shan, W.; Shi, X.; Zhang, C. Influence of sulfation on iron titanate catalyst for the selective catalytic reduction of NO_x with NH_3. *Appl. Catal. B Environ.* **2011**, *103*, 369–377. [CrossRef]
6. Jiang, B.Q.; Deng, B.Y.; Zhang, Z.Q.; Wu, Z.L.; Tang, X.J.; Yao, S.L.; Lu, H. Effect of Zr Addition on the Low-Temperature SCR Activity and SO_2 Tolerance of Fe-Mn/Ti Catalysts. *J. Phys. Chem. C* **2014**, *118*, 14866–14875. [CrossRef]
7. Shen, Y.S.; Su, Y.; Ma, Y.F. Transition metal ions regulate the catalytic performance of $Ti_{0.8}M_{0.2}Ce_{0.2}O_{2+x}$ for the NH_3-SCR of NO: The acidic mechanism. *RSC Adv.* **2015**, *5*, 7597–7603. [CrossRef]
8. Wan, Y.P.; Zhao, W.R.; Tang, Y.; Li, L.; Wang, H.J.; Cui, Y.L.; Gu, J.L.; Li, Y.S.; Shi, J.L. Ni-Mn bi-metal oxide catalysts for the low temperature SCR removal of NO with NH_3. *Appl. Catal. B Environ.* **2014**, *118–149*, 114–122. [CrossRef]
9. Zeng, Z.; Lu, P.; Li, C.T.; Zeng, G.M.; Jiang, X.; Zhai, Y.B.; Fan, X.P. Selective catalytic reduction (SCR) of NO by urea loaded on activated carbon fibre (ACF) and CeO_2/ACF at 30 °C: The SCR mechanism. *Environ. Technol.* **2012**, *33*, 1331–1337. [CrossRef] [PubMed]
10. Zhan, S.H.; Qiu, M.Y.; Yang, S.S.; Zhu, D.D.; Yu, H.B.; Li, Y. Facile preparation of MnO_2 doped Fe_2O_3 hollow nanofibers for low temperature SCR of NO with NH_3. *J. Mater. Chem. A* **2014**, *2*, 20486–20493. [CrossRef]
11. Chang, H.; Li, J.; Yuan, J.; Chen, L.; Dai, Y.; Arandiyan, H.; Xu, J.; Hao, J. Ge, Mn-doped CeO_2-WO_3 catalysts for NH_3-SCR of NO*x*: Effects of SO_2 and H_2 regeneration. *Catal. Today* **2013**, *201*, 139–144. [CrossRef]
12. Grzybek, T.; Klinik, J.; Motak, M.; Papp, H. Nitrogen-promoted active carbons as catalytic supports: 2. The influence of Mn promotion on the structure and catalytic properties in SCR. *Catal. Today* **2008**, *137*, 235–241. [CrossRef]
13. Tian, X.; Xiao, Y.; Zhou, P.; Zhang, W.; Luo, X. Investigation on performance of V_2O_5-WO_3-TiO_2-cordierite catalyst modified with Cu, Mn and Ce for urea-SCR of NO. *Mater. Res. Innov.* **2014**, *18*, 202–206. [CrossRef]

14. Peng, Y.; Li, J.; Si, W.; Li, X.; Shi, W.; Luo, J.; Fu, J.; Crittenden, J.; Hao, J. Ceria promotion on the potassium resistance of MnO*x*/TiO_2 SCR catalysts: An experimental and DFT study. *Chem. Eng. J.* **2015**, *269*, 44–50. [CrossRef]
15. Moosavi, E.S.; Seyed, A.; Dastgheib, S.A.; Karimzadeh, R. Adsorption of Thiophenic Compounds from Model Diesel Fuel Using Copper and Nickel Impregnated Activated Carbons. *Energies* **2012**, *5*, 4233–4250. [CrossRef]
16. Jiang, X.; Lu, P.; Li, C.; Zeng, Z.; Zeng, G.; Hu, L.; Mai, L.; Li, Z. Experimental study on a room temperature urea-SCR of NO over activated carbon fibre-supported CeO_2-CuO. *Environ. Technol.* **2013**, *34*, 591–598. [CrossRef] [PubMed]
17. Jing, W.; Guo, Q.; Hou, Y.; Ma, G.; Han, X.; Huang, Z. Catalytic role of vanadium(V) sulfate on activated carbon for SO_2 oxidation and NH_3-SCR of NO at low temperatures. *Catal. Commun.* **2014**, *56*, 23–26. [CrossRef]
18. Guo, Q.; Jing, W.; Hou, Y.; Huang, Z.; Ma, G.; Han, X.; Sun, D. On the nature of oxygen groups for NH_3-SCR of NO over carbon at low temperatures. *Chem. Eng. J.* **2015**, *270*, 41–49. [CrossRef]
19. Garcia-Cuello, V.S.; Giraldo, L.; Moreno-Pirajan, J.C. Textural Characterization and Energetics of Porous Solids by Adsorption Calorimetry Textural Characterization and Energetics of Porous Solids by Adsorption Calorimetry. *Energies* **2011**, *4*, 928–947. [CrossRef]
20. Habib, M.A.; Badr, H.M.; Ahmed, S.F.; Ben-Mansour, R.; Mezghani, K.; Imashuku, S.; la O', G.J.; Shao-Horn, Y.; Mancini, N.D.; Mitsos, A.; *et al*. A review of recent developments in carbon capture utilizing oxy-fuel combustion in conventional and ion transport membrane systems. *Int. J. Energy Res.* **2011**, *35*, 741–764. [CrossRef]
21. Scheffknecht, G.; Al-Makhadmeh, L.; Schnell, U.; Maier, J. Oxy-fuel coal combustion—A review of the current state-of-the-art. *Int. J. Greenh. Gas Control* **2011**, *5*, S16–S35. [CrossRef]
22. Zheng, B.B.; Xu, J.P. Carbon Capture and Storage Development Trends from a Techno-Paradigm Perspective. *Energies* **2014**, *7*, 5221–5250. [CrossRef]
23. Hudson, M.R.; Queen, W.L.; Mason, J.A.; Fickel, D.W.; Lobo, R.F.; Brown, C.M. Unconventional, Highly Selective CO_2 Adsorption in Zeolite SSZ-13. *J. Am. Chem. Soc.* **2012**, *134*, 1970–1973. [CrossRef] [PubMed]
24. Kim, Y.J.; Min, K.M.; Lee, J.K.; Hong, S.B.; Cho, B.K.; Nam, I.-S. Effect of CO_2 on the $DeNO_x$ Activity of a Small Pore Zeolite Copper Catalyst for NH_3/SCR. *ChemCatchem* **2014**, *6*, 1186–1189.
25. Magnusson, M.; Fridell, E.; Ingelsten, H.H. The influence of sulfur dioxide and water on the performance of a marine SCR catalyst. *Appl. Catal. B Environ.* **2012**, *111*, 20–26. [CrossRef]
26. Forzatti, P.; Nova, I.; Tronconi, E.; Kustov, A.; Thogersen, J.R. Effect of operating variables on the enhanced SCR reaction over a commercial V_2O_5-WO_3/TiO_2 catalyst for stationary applications. *Catal. Today* **2012**, *184*, 153–159. [CrossRef]
27. Huang, H.L.; Shan, W.P.; Yang, S.J.; Zhang, J.H. Novel approach for a cerium-based highly-efficient catalyst with excellent NH_3-SCR performance. *Catal. Sci. Technol.* **2014**, *4*, 3611–3614. [CrossRef]
28. Kim, M.K.; Kim, P.S.; Cho, B.K.; Nam, I.S.; Oh, S.H. Enhanced NO_x reduction and byproduct removal by (HC plus OHC)/SCR over multifunctional dual-bed monolith catalyst. *Catal. Today* **2012**, *184*, 95–106. [CrossRef]
29. Lei, Z.; Han, B.; Yang, K.; Chen, B. Influence of H_2O on the low-temperature NH_3-SCR of NO over V_2O_5/AC catalyst: An experimental and modeling study. *Chem. Eng. J.* **2013**, *215*, 651–657. [CrossRef]
30. Pan, S.; Luo, H.; Li, L.; Wei, Z.; Huang, B. H_2O and SO_2 deactivation mechanism of MnO_x/MWCNTs for low-temperature SCR of NO_x with NH_3. *J. Mol. Catal. A Chem.* **2013**, *377*, 154–161. [CrossRef]
31. Smith, M.A.; Depcik, C.D.; Hoard, J.W.; Bohac, S.V.; Assanis, D.N. Modeling of SCR NH_3 Storage in the Presence of H_2O. In Proceedings of the ASME 2011 Internal Combustion Engine Division Fall Technical Conference, Morgantown, WV, USA, 2–5 October 2011.
32. Chang, H.; Chen, X.; Li, J.; Ma, L.; Wang, C.; Liu, C.; Schwank, J.W.; Hao, J. Improvement of Activity and SO_2 Tolerance of Sn-Modified MnO*x*-CeO_2 Catalysts for NH_3-SCR at Low Temperatures. *Environ. Sci. Technol.* **2013**, *47*, 5294–5301. [CrossRef] [PubMed]
33. Wang, X.; Jiang, L.; Wang, J.; Wang, R. Ag/bauxite catalysts: Improved low-temperature activity and SO_2 tolerance for H_2-promoted NH_3-SCR of NO_x. *Appl. Catal. B Environ.* **2015**, *165*, 700–705. [CrossRef]
34. Cha, J.S.; Choi, J.C.; Ko, J.H.; Park, Y.K.; Park, S.H.; Jeong, K.E.; Kim, S.S.; Jeon, J.K. The low-temperature SCR of NO over rice straw and sewage sludge derived char. *Chem. Eng. J.* **2010**, *156*, 321–327. [CrossRef]

35. Singh, S.; Nahil, M.A.; Sun, X.; Wu, C.; Chen, J.; Shen, B.; Williams, P.T. Novel application of cotton stalk as a waste derived catalyst in the low temperature SCR-deNO_x process. *Fuel* **2013**, *105*, 585–594. [CrossRef]
36. Smirniotis, P.G.; Sreekanth, P.M.; Peña, D.A.; Jenkins, R.G. Manganese Oxide Catalysts Supported on TiO_2, Al_2O_3, and SiO_2: A Comparison for Low-Temperature SCR of NO with NH_3. *Ind. Eng. Chem. Res.* **2006**, *45*, 6436–6443. [CrossRef]
37. Shen, B.X.; Ma, H.Q.; He, C.; Zhang, X.P. Low temperature NH_3–SCR over Zr and Ce pillared clay based catalysts. *Fuel Process. Technol.* **2014**, *119*, 121–129.
38. Jiang, B.; Liu, Y.; Wu, Z. Low-temperature selective catalytic reduction of NO on MnO_x/TiO_2 prepared by different methods. *J. Hazard. Mater.* **2009**, *162*, 1249–1254. [CrossRef] [PubMed]
39. Xie, J.; Fang, D.; He, F.; Chen, J.; Fu, Z.; Chen, X. Performance and mechanism about MnO_x species included in MnOx/TiO_2 catalysts for SCR at low temperature. *Catal. Commun.* **2012**, *28*, 77–81. [CrossRef]
40. Qi, G.; Yang, R.T. Performance and kinetics study for low-temperature SCR of NO with NH_3 over MnO_x-CeO_2 catalyst. *J. Catal.* **2003**, *217*, 434–441. [CrossRef]
41. Kijlstra, W.S.; Brands, D.S.; Poels, E.K.; Bliek, A. Mechanism of the selective catalytic reduction of NO by NH_3 over MnO_x/Al_2O_3: I. Adsorption and desorption of the single reaction components. *J. Catal.* **1997**, *171*, 208–218. [CrossRef]
42. Huang, H.Y.; Yang, R.T. Removal of NO by reversible adsorption on Fe-Mn based transition metal oxides. *Langmuir* **2001**, *17*, 4997–5003. [CrossRef]
43. Yang, X.; Zhao, B.; Zhuo, Y.; Chen, C.; Xu, X. Effects of water vapor, CO_2 and SO_2 on the NO reduction by NH_3 over sulfated CaO. *Korean J. Chem. Eng.* **2011**, *28*, 1785–1790. [CrossRef]
44. Garcia-Bordeje, E.; Pinilla, J.L.; Lazaro, M.J.; Moliner, R. NH_3-SCR of NO at low temperatures over sulphated vanadia on carbon-coated monoliths: Effect of H_2O and SO_2 traces in the gas feed. *Appl. Catal. B Environ.* **2006**, *66*, 281–287. [CrossRef]